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<p>(21) International Application Number: PCT/FI98/00554</p> <p>(22) International Filing Date: 24 June 1998 (24.06.98)</p> <p>(30) Priority Data:</p> <table border="0"> <tr> <td>972727</td> <td>24 June 1997 (24.06.97)</td> <td>FI</td> </tr> <tr> <td>972728</td> <td>24 June 1997 (24.06.97)</td> <td>FI</td> </tr> </table> <p>(71) Applicant (for all designated States except US): BOREALIS A/S [DK/DK]; Lyngby Hovedgade 96, DK-2800 Lyngby (DK).</p> <p>(72) Inventors; and</p> <p>(75) Inventors/Applicants (for US only): HARLIN, Ali [FI/FI]; Kärppärinne 1, FIN-01450 Vantaa (FI). AALTONEN, Päivi [FI/FI]; Kuhatiehde 1 B 11, FIN-02170 Espoo (FI). ALASTALO, Kauno [FI/FI]; Karjapolku 4, FIN-06400 Porvoo (FI). KIVELÄ, Jouni [FI/FI]; Sturenkatu 37 - 41 A 3, FIN-00550 Helsinki (FI). KORHONEN, Esa [FI/FI]; Keinupolku 2 E 19, FIN-06400 Porvoo (FI).</p> <p>(74) Agents: LAINE, Seppo et al.; Seppo Laine Oy, Lönnrotinkatu 19 A, FIN-00120 Helsinki (FI).</p>	972727	24 June 1997 (24.06.97)	FI	972728	24 June 1997 (24.06.97)	FI	<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report.</p>
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972728	24 June 1997 (24.06.97)	FI					
<p>(54) Title: PROCESS FOR PREPARING PROPYLENE POLYMERS</p> <p>(57) Abstract</p> <p>Described herein is a process for preparing propylene copolymers. The process comprises the steps of polymerizing propylene with comonomers in at least one slurry reactor and at least one gas phase reactor, at least 10 % of the polymer-product being produced in the gas phase reactor(s); recovering from the slurry reactor a copolymerization product containing unreacted monomers and conducting the copolymerization product to a first gas phase reactor essentially without recycling of the unreacted monomers to the slurry reactor before the gas phase reactor. The process will provide high randomness copolymers, which are very soft, and copolymers having improved impact resistance.</p>							

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PROCESS FOR PREPARING PROPYLENE POLYMERS

Background of the Invention

Field of the Invention

5 The present invention relates to the production of propylene based homopolymers and copolymers having a high comonomer content as well as impact modified polymers of propylene. In particular, the present invention concerns a process for preparing propylene
10 polymers in a reactor system comprising a combination of at least one slurry reactor and at least one gas phase reactor.

Description of Related Art

15 The softness, impact resistance and heat sealing properties of propylene-based polymers can be increased by copolymerizing propylene with other olefins, such as ethylene, i-butylene and the like. Both bulk and gas phase processes have been employed. However, the comonomers used during polymerization cause swelling of the polymers in the polymerization medium of bulk processes. As a result, when swollen and soft polymer
20 particles are flashed after polymerization, the morphology of the particles is destroyed and the bulk density of the powderized polymer becomes very low. At the same time amorphous material accumulates on the surfaces of the powder. Sticky low-density material agglomerates easily on the walls in the flash tank and causes problems during transportation. These problems increase when the proportion of comonomers increases.

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For this reason, in the prior art the polymerization has mainly been carried out by using gas phase processes. These processes have thus been proposed for the production of sticky, but fluidizable products (EP 0 237 003) and for rubbery products, e.g. EPR and EPDM, (EP 0 614 917). In said processes, the gas velocity of the fluidized bed reactor is sufficient
30 to cause the particles to separate and act as a fluid. However, the polymer in the fluid bed reactor is passed through essentially in a plug flow mode.

Gas phase processes are also favoured for high comonomer content products, cf. EP 0 674 991, EP 0 584 574, EP 0 605 001 and EP 0 704 464.

However, a problem relating to gas phase reactors is formed by their long residence times which means long transition times and possible productions losses. This is especially true for multireactor processes. Catalyst productivity in a gas phase process is low, which means higher catalyst and production costs.

In order to draw benefits from the different advantages of the slurry bulk and the gas phase reactors, respectively, some combinations of bulk and gas phase reactors for preparing copolymers of propylene have been suggested in the art. However, to date, none of the prior art processes meets the requirements for flexibility and low production costs dictated by the production of large varieties of polyolefin qualities using one and the same process configuration. In particular, recycling of rather large amounts of unreacted monomers to the slurry reactor, which is a typical feature of the known processes, impairs the loop reactor dynamics and slows up the transition to novel product qualities.

An improved two-stage process for polymerization of propylene in a combination of a loop reactor and a gas phase reactor is disclosed in US Patent No. 4,740,550. The main object of US 4,740,550 is to provide a process for preparing a block copolymer of high quality by feeding homopolymer with narrow residence time distribution to the block copolymerization stage. The process disclosed comprises the following stages: a first stage consisting of homopolymerization in a bulk loop reactor, a second stage homopolymerization in a gas phase reactor, fines removal in a cyclone between the first and second stage, and, finally, impact copolymerization in an additional gas phase reactor.

Before the polymerization product of the loop reactor is fed into the gas phase the fines fraction is removed and circulated back to the loop reactor. Together with the fines a part of the monomers from the gas phase reactor is recycled directly to the first stage loop reactor.

There are some considerable problems related to this prior art. Thus, if all fines are removed from the reactor outlet of the loop reactor and circulated back to the loop reactor, there is a considerable risk that the loop reactor eventually will be filled with inactive catalyst or slightly polymerized dead fines. On the other hand, if a portion of the fines stream would be combined with the product from the last reactor this might cause inhomogeneity problems in the final product. Further, if a portion of the fines stream is separately collected and blended with a separate homopolymer as also suggested in US 4,740,550, this leads to complicated and economically unacceptable operation.

Summary of the Invention

It is an object of the present invention to eliminate the problems related to the prior art of single and multiple-reactor processes and to provide a novel process for preparing homo- and copolymers of propylene.

It is another object of the invention to provide a highly versatile process which can be used for preparing a wide range of different (co)polymer products of propylene.

These and other objects, together with the advantages thereof over known processes, which shall become apparent from specification which follows, are accomplished by the invention as hereinafter described and claimed.

The process according to the present invention is based on a combination of at least one slurry reactor and at least one gas phase reactor connected in series, in that order, to form a cascade. Propylene (co)polymers are prepared in the presence of a catalyst at elevated temperature and pressure. According to the invention, the polymerization product of at least one slurry reactor, containing unreacted monomers, is conducted to the first gas phase reactor with minimum or no recycling of monomer back to the slurry reactor. In connection with the present invention it has been found that impact copolymers of high quality can be produced with a two-stage homopolymerization followed by a impact copolymerization step without any fines removal and circulation either after the first or second stage copolymerization. In the present invention, it is possible to minimize the amount of

circulation by using the specific sequence of reactors and by selecting the relative amounts produced in each reactor with that object in mind.

According to another aspect of the invention, at least one slurry reactor and at least one gas phase reactor connected in series are employed as a reactor system, the at least one slurry reactor being a bulk loop reactor operated at high or super critical temperature, and the content of the slurry reactor, including the copolymer product and reaction medium containing unreacted monomers, is led directly into the gas phase reactor fluidized bed using a conduit interconnecting the slurry reactor and the gas phase reactor.

More specifically, the process according to the present invention is mainly characterized by what is stated in the characterizing part of claim 1.

The invention achieves a number of considerable advantages. With the present arrangement it has been found that the monomers fed into the first reactor can, to a large extent or fully, be consumed in the gas phase reactor(s) after the slurry reactor. This is possible due to gas phase operation with small amount of gas leaving with the polymer product. The loop reactor dynamics in the cascade provides fast transitions and high productivity. Fast start-ups are also possible because the gas phase bed material is available directly from the loop reactor. With the loop and gas phase reactor cascade it is possible to produce a large variety of different broad molecular weight distribution or bimodal products. The at least one gas phase reactor provides high flexibility in the reaction rate ratio between the first and second part of the product because of adjustable bed level and reaction rate. Further, the gas phase reactor having no solubility limitations makes it possible to produce polymers of high and very high comonomer content.

The loop-gas phase reactor combination have greatly reduced residence times and production losses in comparison to gas phase - gas phase multireactor processes.

Brief Description of the Drawings

Figure 1 depicts in a schematic fashion the process configuration of a first preferred embodiment of the invention; and

5 Figure 2 depicts in a schematic fashion the process configuration of a second preferred embodiment of the invention.

Detailed Description of the Invention**10 Definitions**

For the purpose of the present invention, "slurry reactor" designates any reactor, such as a continuous or simple stirred tank reactor or loop reactor, operating in bulk or slurry and in which the polymer forms in particulate form. "Bulk" means a polymerization in reaction
15 medium that comprises at least 60 wt-% monomer. According to a preferred embodiment the slurry reactor comprises a bulk loop reactor.

By "gas phase reactor" is meant any mechanically mixed or fluid bed reactor. Preferably the gas phase reactor comprises a mechanically agitated fluid bed reactor with gas
20 velocities of at least 0.2 m/sec.

"High temperature polymerization" stands for polymerization temperatures above a limiting temperature of 80 °C known to be harmful for high yield catalysts of related prior art. At high temperatures the stereospecificity of the catalyst and the morphology of the
25 polymer powder can be lost. This does not take place with the particularly preferred type of catalysts used in the invention which is described below. The high temperature polymerization takes place above the limiting temperature and below the corresponding critical temperature of the reaction medium.

30 "Super critical polymerization" designates polymerization that takes place above a corresponding critical temperature and pressure of the reaction medium.

By "direct feed" is meant a process in which the content of a slurry reactor, comprising the polymerization product and the reaction medium, is lead directly to the fluidized bed of a gas phase reactor.

- 5 "Reaction zone " stands for one or several reactors of similar type connected in series producing the same type or characteristics of polymer.

The expressions "essentially without monomer recycling" and "with minimum or no monomer recycling" are synonymously used to indicate that no more than about 30 wt-%, preferably less than 20 wt-% and in particular nothing of the monomers is recycled to the slurry process. By contrast, in a normal slurry process, 50 wt-% or more of the monomer is recycled.

The overall process

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The present invention concerns a multistage process consisting of a bulk reaction zone including at least one slurry reactor, and a gas phase reaction zone including at least one gas phase reactor in cascade after at least one slurry reactor with a minimum or no recycling of monomer back to the first reactor and with direct feed or indirect feed to the gas phase for homo- or copolymerizing propylene.

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In the direct feed process the content of the slurry reactor, the polymerization product and reaction medium, is conducted directly to the fluidized bed reactor. The product outlet from the slurry reactor can be discontinuous, or preferably continuous. The slurry is led as such without separation of any gases or particle streams based on different particle size. No particles are retured to the preceding reactor. Optionally, the line between the slurry reactor and the gas phase reactor can be heated in order to evaporate only a part or all of the reaction medium before it enters the gas phase reactor polymer bed.

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30 The reaction is continued in the gas phase reactor(s). All or practically all (at least about 90 %) of the monomer entering the gas phase from the slurry reactor is part of the reactor gas inventory until it is converted into the polymer.

In two reactor operation the polymer leaving the gas phase reactor with the outlet system enters a solid/gas separation unit. The polymer from the bottom is fed to further processing steps and the gas is compressed and circulated back to the gas phase reactor after purification steps. Typically light inerts, such as methane and ethane, and heavier inerts such as propane and oligomers are removed in these purification steps. The purification can be performed with distillation or membrane separation. In case of distillation the monomers are circulated back to the gas phase reactor mainly as liquid.

In three reactor operation the polymer leaving the 1st gas phase reactor with the outlet system enters a solid/gas separation unit. The polymer from the bottom is fed further to 2nd gas phase reactor and the gas is compressed and circulated back to the 1st gas phase reactor after purification steps. Typically light inerts, such as methane and ethane, and heavier inerts such as propane and oligomers are removed in these purification steps. The purification can be performed with distillation or membrane separation. In case of distillation the monomers are circulated back to the gas phase reactor mainly as liquid.

Optionally in three reactor operation the polymer leaving the 1st gas phase reactor with the outlet system enters the 2nd gas phase reactor directly with the accompanying gas.

In three reactor operation the polymer leaving the 2nd gas phase reactor with the outlet system enters a solid/gas separation unit. The polymer from the bottom is fed to further processing steps and the gas is compressed and partly circulated back to the 2nd gas phase reactor directly, partly after purification steps. Typically light inerts, such as methane and ethane, and heavier inerts such as propane and oligomers are removed in these purification steps. The purification can be performed with distillation or membrane separation. In case of distillation an ethylene rich stream is circulated back to the 2nd gas phase reactor and a propylene-propane stream is fed to propane and oligomers removal steps.

The polymerization products are obtained by using a catalyst. The catalyst can be any catalyst providing adequate activity at elevated temperature. The preferred catalyst system used comprises a high yield Ziegler-Natta catalyst having catalyst component, a co-catalyst component, an external donor and, optionally, an internal donor. Another preferred catalyst

system is a metallocene-based catalyst, e.g. having a bridged ligand structure giving high stereoselectivity, and which is impregnated on a carrier or support in the form of an activated complex.

5 The polymerization temperature is at least 60 °C, preferably at least 65 °C. The slurry reactor is operated at elevated pressure at least 35 bar up to 100 bar, and the gas phase reactor(s) at least 10 bar up to dew point pressure. Alternatively any reactor of the reactors in the series can be operated above the critical temperature and pressure.

10 Propylene and optionally one or more other C₂ to C₁₆ olefins, e.g. ethylene, 1-butene, 4-methyl-1-pentene, 3-methyl-1-butene, 1-hexene, 1-octene, 1-decene, dienes, or cyclic olefins, e.g. vinylcyclohexane or cyclopentene, is subjected to polymerization and copolymerization, respectively, in a plurality of polymerization reactors connected in series. The comonomer olefin(s) can be used in any of the reactors. Different amounts of
15 hydrogen can be used as a molar mass modifier or regulator in any or every reactor.

The desired (co)polymers of propylene can be recovered from the product separation means of the gas phase reaction zone.

20 The catalyst

The polymerization products are obtained by using a catalyst. As catalyst any stereo-specific catalyst for propylene can be used, which has high yield and useful polymer properties e.g. isotacticity and morphology at the high temperature and possible
25 supercritical polymerization. The preferred catalyst system used comprises a high yield Ziegler-Natta catalyst having catalyst component, a cocatalyst component, optionally, an external donor and an internal donor. Another preferred catalyst system is a metallocene catalyst having a bridged ligand structure giving high stereoselectivity, and which has an active complex impregnated on a carrier. Finally, the catalyst is preferably any other
30 catalyst providing adequate activity at elevated temperature.

Examples of suitable systems are described in, for example, FI Patents Nos. 86866, 96615 and 88047, 88048 and 88049.

One particularly preferable catalyst, which can be used in the present invention is disclosed in FI Patent No. 88047. Another preferred catalyst is disclosed in FI Patent Application No. 963707.

Further preferred catalysts are disclosed in PCT/FI 97/00191 and PCT/FI97/00192.

10 **Prepolymerization**

The catalyst can be prepolymerized prior to feeding into the first polymerization reactor of the series. During prepolymerization the catalyst components are contacted with a monomer, such as an olefin monomer, before feeding into the reactor. Examples of suitable systems are described in, for example, FI Patent Application No. FI 961152.

It is also possible to carry out the prepolymerization in the presence of a viscous substance, such as an olefinic wax, to provide a prepolymerized catalyst which is stable during storage and handling. The catalyst prepolymerized in wax will allow for easy dosing of the catalyst into the polymerization reactors. Examples of suitable systems are described in, for example, FI Patent No. 95387. Typically about 1 part of catalyst is used for a maximum of 4 parts of polymer.

The monomer used for prepolymerization can be selected from the group consisting of propylene, 1-butene, 4-methyl-1-pentene, 3-methyl-1-butene, vinylcyclohexane, cyclopentene, 1-hexene, 1-octene, and 1-decene.

The prepolymerization can be performed batchwise in wax or in a continuous prepolymerization reactor or in a continuous plug flow type prepolymerization reactor.

Polymerization

The invention is based on the combination of at least one slurry reactor and at least one gas phase reactor connected in series, called a cascade.

5

The equipment of the polymerization step can comprise polymerization reactors of any suitable type. The slurry reactor can be any continuous or simple stirred tank reactor or loop reactor operating in bulk or slurry and the polymer forms in particular form in the reactor. Bulk means a polymerization in reaction medium that comprises of at least 60 % (w/w) monomer. The gas phase reactor can be any mechanically mixed or fluid bed reactor. According to the present invention the slurry reactor is preferably a bulk loop reactor and the gas phase reactor is a fluidized bed type reactor with a mechanical stirrer.

10

Any reactor in the process can be a super critical polymerization reactor.

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The production split between the slurry reactor and the 1st gas phase reactor is typically 67:33-50:50 when monomer recycling back to the slurry reactor is allowed. By contrast, the production in the slurry reactor is less than or equal to the production in the first gas phase reactor when no recycling back to the slurry reactor is required. In all the cases the production in the slurry reactor is more than 10 %. Thus, according to a preferred embodiment, 10 to 70 wt-%, preferably 20 to 65 wt-%, in particular 40 to 60 wt-% of the polymer is prepared in the slurry reaction zone and no monomer is recycled to the slurry reactor zone. When 50 % to 67 % of the polymer is prepared in the slurry reaction zone, a small amount of the monomer can be recycled to the slurry reactor from the gas phase reaction zone.

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According to the invention, the polymerization process comprises at least the following steps of

- subjecting propylene and optionally other olefins to polymerization or copolymerization in a first slurry polymerization zone or reactor,
- recovering the first polymerization product from the first reaction zone with the reaction medium,

30

- directly or indirectly feeding the first polymerization product into a gas phase polymerization zone or reactor,
- optionally feeding additional propylene and/or comonomer(s) to the second reaction zone,
- 5 · subjecting the excess propylene and/or comonomers from 1st zone and additional propylene and/or comonomer(s) to a second polymerization reaction in the presence of the first polymerization product to produce a second polymerization product,
- recovering the polymerization product from second reaction zone, and
- separating and recovering the polypropylene from the second reaction product.

10

Additionally the process can also comprise one or more of the following additional steps

- prepolymerizing catalyst with one or more monomer(s),
- separating gas from the second reaction zone product,
- feeding the recovered polymerization product of the earlier zones to a third or fourth
- 15 reaction zone or reactor,
- optionally feeding additional propylene and/or comonomer(s) to the third and fourth reaction zone,
- subjecting the excess propylene and/or comonomer(s) and additional propylene and/or comonomers to third and fourth polymerization reaction in the presence of the
- 20 polymerization product of the earlier zones to produce a third or fourth polymerization product, and
- recovering the polymerization product from the third or fourth reaction zone, and
- separating and recovering the polypropylene from the third or fourth reaction product.

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In the first step of the process, propylene with the optional comonomer(s) together with the activated catalyst complex and optional cocatalyst and other aid components are fed into the first polymerization reactor. The catalyst can be prepolymerized or it is prepolymerized before feeding to the process. Along with the afore-mentioned components hydrogen as a molar mass regulator can be fed into the reactor in the amount required for achieving the

30 desired molar mass of the polymer. In the embodiment of no circulation back to the slurry reactor only fresh monomer is fed into the first reactor.

Alternatively, in the embodiment of minimum recycling of the monomer back to the slurry reactor, the feed of the reactor can consist of the recycled monomer from the following reactor(s) passed through a recovery system, if any, together with added fresh monomer, hydrogen, optional comonomer(s) and catalyst components.

5

In all of the embodiments the presence of propylene, optional comonomer(s), cocatalyst and other aid components, the activated catalyst complex will polymerize and form a product in particulate form in the slurry reactor, i.e. polymer particles, which are suspended in the fluid circulated in the reactor.

10

The polymerization medium typically comprises the monomer and optionally a hydrocarbon, and the fluid is either liquid or gaseous. In the case of slurry reactor, in particular a loop reactor, the fluid is liquid and the suspension of polymer is circulated continuously through the slurry reactor, whereby more suspension of polymer in particle form in hydrocarbon medium or monomer will be produced. According to preferred embodiment, the first polymerization or copolymerization reaction is carried out in a reaction medium mainly consisting propylene. Preferably at least 60 weight percent of the medium is propylene.

15

The conditions of the slurry reactor are selected so that at least 10 wt-%, preferably at least 12 wt-% of the whole production is polymerised in the first slurry reactor. The temperature is in the range of 40 to 110 °C, preferably 50 to 100 °C, and even more preferably for homopolymers and high randomness copolymer 80 to 100 °C and for copolymers of high comonomer content 60 to 75 °C. The reaction pressure is in the range of 30 to 100 bar, preferably 35 to 80 bar based on the vapour pressure of the reaction medium.

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In slurry polymerization zone more than one reactor can be used in series. In such a case the polymer suspension in an inert hydrocarbon or in monomer produced in the 1st slurry reactor is fed without separation of inert components and monomers periodically or continuously to the following slurry reactor, which acts at lower pressure than the previous slurry reactor.

30

The polymerization heat is removed by cooling the reactor with a cooling jacket. The residence time in the slurry reactor must be at least 10 minutes, preferably 20-100 min for obtaining a sufficient degree of polymerization. This is necessary to achieve polymer yields of at least 40 kg PP/g cat. It is also advantageous to operate the slurry reactor with high solid concentrations, e.g. 50 % for homopolymers and 35 or 40 % for some copolymers when the particles are swelling. If the solid concentration in the loop reactor is too low, the amount of reaction medium conducted to the second reaction zone or gas phase reactor is increasing.

- 10 The content of the slurry reactor, the polymerization product and reaction medium, is led directly to the gas phase reactor fluidized bed.

The second reactor is preferably a gas phase reactor, wherein propylene and optionally comonomer(s) are polymerized in reaction medium which consists of gas or vapour.

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The gas phase reactor can be an ordinary fluidized bed reactor, although other types of gas phase reactors can be used. In a fluidized bed reactor, the bed consists of the formed and growing polymer particles as well as still active catalyst come along with the polymer fraction. The bed is kept in a fluidized state by introducing gaseous components, e.g. monomer on such flow rate (at least 0.2 m/s) which make the particles act as a fluid. The fluidizing gas can contain also inert gases, like nitrogen and also hydrogen as a modifier. In the invention it is not recommendable to use unnecessary inert gases, which may cause problems in the recovery section.

20

- 25 The gas phase reactor used can be operated in the temperature range of 50 to 115 °C, preferably between 60 and 110 °C and reaction pressure between 10 and 40 bar and the partial pressure of the monomer is preferably between 2 and 30 bar or more, but always below the dew point pressure.

- 30 According to one preferred embodiment, no fresh propylene is fed to the first gas phase reactor other than what is required for various flushings.

The pressure of the second polymerization product including the gaseous reaction medium is then reduced after the first gas phase reactor in order to separate part of the gaseous and possible volatile components (e.g. heavy comonomers and compounds used for catalyst feeds) of the product e.g. in a flash tank. The overhead gas stream is recirculated through the recovery system back to the first gas phase reactor or partly to the first gas phase reactor and partly to the slurry reactor. Some of the monomers, typically the heavier comonomers, can be recycled to the bulk reaction zone.

If desired, the polymerization product can be fed into a second gas phase reactor and subjected to a third polymerization reaction to produce a modified polymerization product from which the polypropylene is separated and recovered. The third polymerization reaction is carried out in a gas phase reactor in the presence of comonomers which give the third polymerization product properties, e.g. improved impact strength, ductility or softness. Typically, part of the gases coming from the first gas phase reactor are removed in a pressure reduction step before the second gas phase reactor. The removed gases are compressed to the recovery section and handled as already described in the two reactor case. Alternatively, the second product can be transferred directly to the third reactor.

Generally, if copolymers are produced by means of the present invention they contain at least 0.5 wt-% of comonomer(s), in particular at least about 2 wt-% and preferably up to 20 wt-% of at least one comonomer. A typical comonomer content of a copolymer fed to the first gas phase reactor is about 2 to 16 wt-%. The copolymers produced can exhibit properties of high randomness (very soft copolymers).

In particular, the polymerization product is fed into the second gas phase reactor for providing a rubbery copolymer by a third (co)polymerization reaction to produce a modified polymerization product. This third polymerization reaction will give the polymerization product properties of e.g. improved impact strength. The step of providing an elastomer can be performed in various ways. Thus, preferably an elastomer is produced by copolymerizing at least propylene and ethylene into an elastomer. The conditions for the copolymerization are within the limits of conventional EPM production conditions such as they are disclosed, e.g., in Encyclopedia of Polymer Science and Engineering, Second

Edition, Vol. 6, p.545-558. A rubbery product is formed if the ethylene repeating unit content in the polymer lies within a certain range. Thus, preferably, ethylene and propylene are copolymerized into an elastomer in such a ratio that the copolymer contains from 10 to 70 % by weight of ethylene units. In particular, the ethylene unit content is from 30 to 50 % by weight of the copolymer propylene/ethylene elastomer. In other words, ethylene and propylene are copolymerized into an elastomer in a molar ratio of ethylene-to-propylene of 30/70 to 50/50.

The elastomer can also be provided by adding a ready-made or natural elastomer to the polymer product of the first gas phase reactor.

The impact modified polypropylene typically contains about 5 to 50 wt-%, in particular about 10 to 45 wt-% and preferably about 15 to 40 wt-% of an elastomer described above.

Typically, the hydrogen concentration of the second reaction product is reduced before the product is fed into the second gas phase in order to enable production of higher molar mass for achieving improved impact properties.

It is further possible to transfer the product of the second gas phase reaction to a third (fourth etc.) polymerization reaction zone, wherein copolymerization is carried out in the presence of comonomers which give the third polymerization modified product properties.

The third and fourth gas phase reactor can be operated at temperatures in the range of 60 to 80 °C, and the reaction pressure can be kept at 10 to 30 bar.

Summarising what has been stated above, one particularly preferred embodiment of the invention comprises (Fig. 1)

- polymerizing propylene in a loop reactor at a pressure of 40 to 80 bar, at a temperature of 80 to 100 °C and hydrogen is used to control the molar mass of the polymerization product,
- recovering the polymerization product from the loop reactor and conducting it to a gas phase reactor fluid bed,

- optionally feeding additional propylene and optional comonomer to the gas phase reactor,
- optionally feeding additional hydrogen to the gas phase reactor to control the hydrogen-to-propylene ratio to provide the desired molecular mass of the polymerization product,
- recovering the polymerization product from the gas phase reactor and conducting it to a flash tank, wherein the pressure of the product is reduced to produce an overhead product containing essentially non-reacted propylene and hydrogen and a bottom product primarily containing polymerized solids,
- recycling the overhead product or at least a major part of it to the gas phase reactor via a recovery section, and
- recovering polypropylene polymer as the bottom product of the flash tank.

According to the second particularly preferred embodiment (Fig. 1):

- propylene and copolymer(s), e.g. ethylene or 1-butene or both, are polymerised in a loop reactor at a pressure of 40 to 80 bar, at a temperature of 60 to 80 °C and hydrogen is used to provide a polymerization product having the desired molar mass,
- the polymerization product from the loop reactor is conducted directly to a gas phase reactor fluid bed,
- optionally additional propylene and comonomer(s) are fed to the gas phase reactor,
- optionally additional hydrogen is fed to the gas phase reactor to control the hydrogen-to-propylene ratio to provide desired molecular mass of the polymerization product,
- the polymerization product is recovered from the gas phase reactor and conducted to a flash tank, wherein the pressure is reduced to produce an overhead product containing essentially non-reacted monomers and hydrogen and a bottom product primarily containing polymerized solids,
- the overhead product or at least a major part of it is recycled to the gas phase reactor via a recovery section, and
- polypropylene polymer is recovered as the bottom product of the flash tank.

According to the third particularly preferred embodiment (Fig. 2):

- propylene and optionally comonomers are polymerised in a loop reactor at a pressure of 40 to 80 bar, at a temperature of 60 to 100 °C and hydrogen is used to control the molar mass of the polymerization product,
- the polymerization product from the loop reactor is recovered and conducted to a gas phase reactor fluid bed,
- optionally additional propylene and optional comonomer is fed to the gas phase reactor,
- additional hydrogen is optionally fed to the gas phase reactor to control the hydrogen-to-propylene ratio to provide desired molecular mass of the polymerization product,
- the polymerization product from the first gas phase reactor is recovered and conducted to an intermediate flash tank, wherein the pressure of the product is reduced to produce an overhead product containing essentially non-reacted monomer(s) and hydrogen and a bottom product primarily containing polymerised solids,
- the overhead product or at least a major part of it is recycled to the first gas phase reactor via a recovery section,
- the polypropylene polymer from the bottom of the intermediate flash tank is fed to a third polymerization reaction via a polymer feed system,
- the third polymerization reaction is carried out in a gas phase reactor in the presence of comonomers,
- the polymerization product from the second gas phase reactor is recovered and conducted to a flash tank, wherein the pressure of the product is reduced to produce an overhead product containing essentially non-reacted monomer(s) and hydrogen and a bottom product containing primarily polymerised solids,
- optionally the polymerization product from the third polymerization can be conducted directly or via a flash tank to a third (fourth etc.) gas phase polymerization reactor, wherein polymerization is carried out in the presence of comonomers.

These above-mentioned two preferred embodiments are also depicted in the attached drawings, which illustrate the particular configuration of process equipment used. The numerals refer to the following pieces of equipment:

5	1; 101	prepolymerization reactor
	30; 130	catalyst reservoir
	31; 131	feeding device
	32; 132	diluent (optional)
	33; 133	catalyst/diluent mixture
10	34; 134	monomer
	35; 135	cocatalyst and possible donors
	40; 140	loop reactor
	42; 142	diluent feed (optional)
	43; 143	monomer feed
15	44; 144	hydrogen feed
	45; 145	comonomer feed (optional)
	46; 146	back to the loop reactor 40; 140 through the line 46; 146
	47; 147	one or several exhaust valve
	150b	flash separator
20	152b	removing line
	60; 160; 160b	gas phase reactor
	61; 161; 161b	gas transfer line
	62; 162; 162b	compressor
	63; 163; 163b	monomer feed
25	64; 164; 164b	comonomer feed
	65; 165; 165b	hydrogen feed
	66; 166; 166b	transfer line
	67; 167	product transfer line
	68; 168	polymer product recovery system, e.g. flash tank
30	69; 169	recovery line
	70; 170	monomer recovery system

Turning to figure 1, it can be noted that catalyst from reservoir 30 is fed to the feeding device 31 together with optional diluent from line 32. The feeding device 31 feeds the catalyst/diluent mixture into the prepolymerization chamber 1 via line 33. Monomer is fed through 34 and cocatalyst and possible donors can be fed into the reactor 1 through conduits 35 or, preferably, the cocatalyst and donor(s) are intermixed and fed in line 35.

From the prepolymerization chamber 1 the prepolymerized catalyst is removed preferably directly through line 36 and transferred to a loop reactor 40. In the loop reactor 40 the

polymerization is continued by adding an optional diluent from the line 42, monomer from line 43, hydrogen from line 44 and an optional comonomer from line 45 through the line 46. An optional cocatalyst can also be introduced into the loop reactor 40.

- 5 From the loop reactor 40 the polymer-hydrocarbon mixture is fed through one or several exhaust valves 47 described in, e.g., FI Patent Applications Nos. 971368 or 971367. There is a direct product transfer 67 from the loop reactor 40 to gas phase reactor 60.

10 In the lower part of the gas phase reactor 60 there is a fluid bed consisting of polymer particles, which will be kept in a fluidized state in an ordinary way by circulating the gases removed from the top of the reactor 60 through line 61, compressor 62 and a heat exchanger (not presented) to the lower part of the reactor 60 in an ordinary way. The reactor 60 is advantageously, but not necessarily, equipped with a mixer (described in FI Patent Application No. 933073, not shown in the figure). To the lower part of the reactor 60 can
15 be led in a well known way monomers from line 63, optionally comonomer from line 64 and hydrogen from the line 65. The product will be removed from the reactor 60 continually or periodically through the transfer line 66 to the flash tank 68. The overhead product of the recovery system is circulated to the gas phase reactor via a monomer recovery system.

20

The embodiment shown in Figure 2 differs from the one in Figure 1 only in the sense that product from gas phase reactor 160 is fed into the additional gas phase reactor 160b. The polymer particles are removed from the flash tank 168 and the polymer feed tank 150b through the removing line 152b to the gas phase reactor 160b. The gas phase reactor is
25 advantageously equipped with a mixer (not shown).

The overhead of the flash separator 168b is recycled partly to the gas phase reactor 160b and partly to the monomer recovery system.

- 30 In both of the above presented embodiments, the numerals 70 and 170 signify separation means, such as membrane unit or stripping columns, which are capable of freeing the recycle monomer of the gas phase reactor(s) (60, 160 and 160b) or of the separators (68,

168 and 168b) from hydrogen and/or light inert hydrocarbons typically having a lower boiling point than the monomer(s).

The polymers

The products produced according to the present invention comprise polypropylene copolymers including polypropylene terpolymers. In particular, it is possible by means of the present invention to produce high randomness copolymers, which are very soft. The copolymers contain at least 0.5 wt-% of a comonomer, in particular at least about 2 wt-% and preferably up to 20 wt-% of a comonomer. A typical comonomer content is about 2 to 12 wt-%. An essential feature of the invention is the high polymerization temperature used, preferably above 75 °C, which will provide a more even comonomer distribution during copolymerizations. The randomness, measured by FTIR, at a polymerization temperature of 60 °C is 69 %, at 65 °C 71 %, and at a polymerization temperature of 75 °C in the first reactor and 80 °C in the second reactor 74 %.

Further products produced by the present invention include impact modified propylene polymers preferably containing a rubbery copolymer, in particular, an ethylene-propylene copolymer, improving the impact resistance of the product. The proportion of the elastomer is about 5 to 40 % by weight of the polypropylene.

The following non-limiting examples illustrate the principles of the present invention.

Example 1

A production scale plant for continuous production of PP-homopolymer was simulated. The plant comprises catalyst, alkyl, donor, propylene feed systems, prepolymerization reactor, loop reactor and a fluidized bed gas phase reactor (GPR).

The catalyst, alkyl, donor and propylene were fed to the prepolymerization reactor. The polymer slurry from the prepolymerization reactor was fed to a loop reactor to which also hydrogen and more propylene was fed. The polymer slurry from the loop reactor and additional hydrogen and propylene was fed to the GPR. The production in the reactors were 300 kg/h in prepolymerization, 15 t/h in loop and 10 t/h in GPR.

The prepolymerization loop reactor was operated at a 56 bar pressure and a 20 °C temperature. The loop reactor was operated at a 55 bar pressure and a 85 °C temperature. The MFR (2.16 kg, 230 °C) of the PP-homopolymer produced in the loop was adjusted to 1 by controlling the hydrogen feed.

5

The GPR was operated at a pressure of 35 bar and a temperature of 85 °C. The MFR (2.16 kg, 230 °C) of the PP-homopolymer taken out of the GPR was adjusted to 13 by controlling the partial pressure of hydrogen. 5 t/h of propene was recirculated from the GPR outlet back to the loop reactor. The once-through conversion of propylene was 83 %.

10

Example 2

A production scale plant for continuous production of PP-copolymer with good impact properties was simulated. The plant comprises catalyst, alkyl, donor, propylene feed systems, prepolymerization reactor, loop reactor and a 2 fluidized bed gas phase reactors (cf. Figure 2).

15

The catalyst, alkyl, donor and propylene were fed to the prepolymerization reactor. The polymer slurry from the prepolymerization reactor was fed to the loop reactor to which also hydrogen and more propylene was fed. The polymer slurry from the loop reactor and additional hydrogen and propylene was fed to the first GPR.

20

Before entering the second GPR the polymer from the first GPR was depressurized. Ethylene and additional propylene was fed to the second GPR.

25

The production in the reactors was 300 kg/h in prepolymerization, 15 t/h in loop and 10 t/h in the first GPR and 6 t/h in the second GPR.

The prepolymerization loop reactor was operated at a pressure of 56 bar and a temperature of 20 °C. The loop reactor was operated at a pressure of 55 bar and a temperature of 85 °C. The MFR (2.16 kg, 230 °C) of the PP-homopolymer produced in the loop was adjusted to 20 by controlling the hydrogen feed.

30

The first GPR was operated at a pressure of 35 bar and at a temperature of 85 °C. The MFR (2.16 kg, 230 °C) of the PP-homopolymer taken out from the first GPR was set at 20 by adjusting the partial pressure of hydrogen. ~~4.3 t/h of propene was~~ recirculated from the GPR outlet back to the loop reactor.

5

The second GPR was operated at a pressure of 20 bar and a temperature of 70 °C. The MFR (2.16 kg, 230 °C) of the PP-copolymer taken out from the second GPR was adjusted to 13 by using the partial pressure of hydrogen as a control means. ~~2.7 t/h of propene was~~ recirculated from the second GPR outlet back to the loop reactor and ~~1.6 t/h ethylene~~ recirculated to the second GPR

10

Example 3

A production scale plant for continuous production of random PP polymer was simulated.

15

The plant comprises a catalyst, alkyl, donor, propylene and ethylene feed systems, prepolymerization reactor, loop reactor and a fluidized bed gas phase reactor (GPR).

The catalyst, alkyl, donor and ~~propylene~~ were fed to the prepolymerization reactor. The polymer slurry from the prepolymerization reactor was fed to the loop reactor. Ethylene, hydrogen and more propylene was fed also fed to the loop. The polymer slurry from the loop reactor and additional hydrogen, ethylene and propylene was fed to GPR. The production rate in the reactors were 300 kg/h during prepolymerization, 15 t/h in the loop and 10 t/h in the GPR.

20

The prepolymerization reactor was operated at a pressure of 56 bar and a temperature of 20 °C. The loop reactor was operated at a pressure of 55 bar and a temperature of 75 °C. The MFR (2.16 kg, 230 °C) of the random-PP produced in the loop was adjusted to 7 by controlling the hydrogen feed, and the ethylene content was adjusted to 3.5 % w/w by the ethylene feed.

30

The GPR was operated at a pressure of 35 bar and a temperature of 80 °C. The MFR (2.16 kg, 230 °C) of the random-PP taken out from the GPR was adjusted to 7 by controlling the

partial pressure of hydrogen, and the ethylene content was set at 3.5 % w/w by adjusting the partial pressure of ethylene. 5 t/h of propene and 33 kg/h ethylene was recirculated from the GPR outlet back to the loop reactor. The once-through conversion of the propylene and ethylene were 83 % and 96 % respectively.

5

Example 4

A production scale plant for continuous production of PP-copolymer with good impact and creep properties was simulated. The plant comprises catalyst, alkyl, donor, ethylene and propylene feed systems, a prepolymerization reactor, a loop reactor, a flash tank and 2 fluidized bed gas phase reactors.

10

15

The catalyst, alkyl, donor and propylene were fed to the prepolymerization reactor. The polymer slurry from the prepolymerization reactor was fed to a loop reactor to which also hydrogen and more propylene was fed. The polymer slurry from the loop reactor was fed to a flash tank, wherein propylene and polymer were separated.

20

The polymer from flash tank was fed to the first GPR. Propylene from flash tank was fed to the first GPR after removal of hydrogen. Ethylene and additional propylene was fed to the first GPR. The polymer from first GPR was fed to the second GPR. Ethylene, some hydrogen and additional propylene were fed to the second GPR.

25

The prepolymerization reactor was operated at a pressure of 56 bar and a temperature of 20 °C. The loop reactor was operated at a pressure of 55 bar and a temperature of 85 °C. The MFR (2.16 kg, 230 °C) of the PP-homopolymer produced in the loop was set at 100 by adjusting the hydrogen feed.

30

The GPR was operated at a pressure of 35 bar and a temperature of 80 °C. The MFR (2.16 kg, 230 °C) of the PP of the GPR was set at 0.4 by controlling the production split between

the reactors and the efficiency of hydrogen removal of flashed propene. ~~Ethylene content~~
was set at 2 % w/w by adjusting the partial pressure of ethylene and controlling the
~~production split between the reactors.~~
production split between the reactors.

- 5 The second GPR was operated at a pressure of 20 bar and a temperature of 70 °C. The
MFR (2.16 kg, 230 °C) of the PP-copolymer in taken out of the second GPR was adjusted
to 0.3 by controlling the partial pressure of hydrogen and by controlling the production
split between the reactors. Minor amounts of propylene were circulated from the second
GPR back to the loop reactor.

10

Example 5

- A production scale plant for continuous production of PP-copolymer with good creep
properties was simulated. The plant comprises catalyst, alkyl, donor, ethylene and
15 propylene feed systems, a prepolymerization reactor, a loop reactor, a flash tank and a
fluidized bed gas phase reactor.

20

The catalyst, alkyl, donor and ~~propylene~~ were fed to prepolymerization reactor. The
polymer slurry from the prepolymerization reactor was fed to a loop reactor to which also
ethylene and more propylene was fed. The polymer slurry from the loop reactor was fed to
a flash tank, wherein monomers and polymer were separated.

25

The polymer from flash tank was fed to the GPR. Propylene from the flash tank was fed to
the GPR after removal of ethylene. Hydrogen and additional propylene were fed to the
GPR.

The production in the reactors were 300 kg/h during prepolymerization, 10 t/h in loop and
10 t/h in the first GPR

30

Example 6

A pilot plant operated continuously was used to produce PP-homopolymer. The plant comprises catalyst, alkyl, donor, propylene feed systems, a prepolymerization reactor, a loop reactor and a fluidized bed gas phase reactor (GPR).

5 The catalyst, alkyl, donor and propylene were fed to the prepolymerization reactor. The polymer slurry from the prepolymerization reactor was fed to a loop reactor to which also hydrogen and more propylene was fed. The polymer slurry from the loop reactor and additional hydrogen and propylene was fed to the GPR.

10 The formed polymer and unreacted propylene were separated after removal of the polymerization product from the GPR.

The catalyst used was a highly active and stereospecific ZN-catalyst made according to U.S. Patent No. 5,234,879. The catalyst was contacted with triethylaluminium (TEA) and
15 dicyclopentylmethoxysilane (DCPDMS) (Al/Ti ratio was 250 and Al/Do 40 (mole)) before feeding to the prepolymerization reactor.

The catalyst was fed according to U.S. Patent No. 5,385,992 and was flushed with propylene to the prepolymerization reactor. The prepolymerization reactor was operated at
20 51 bar pressure, 20 °C temperature and mean residence time of the catalyst at 7 min.

The prepolymerized catalyst propylene and other components were transferred to the loop reactor. The loop reactor was operated at a pressure of 50 bar, a temperature of 80 °C and a mean residence time of the catalyst of 1 h. The MFR (2.16 kg, 230 °C) of the PP-
25 homopolymer produced in the loop was adjusted to 7 by using the hydrogen feed as a control means.

The polymer slurry from the loop reactor was transferred to the GPR. The GPR reactor was operated at a total pressure of 29 bar and a partial pressure of propylene amounting to 21
30 bar. The temperature was 90 °C and the mean residence time of the catalyst was 1 h. The MFR (2.16 kg, 230 °C) of the PP-homopolymer taken out of the GPR was 7 and controlled by adjusting the partial pressure of hydrogen. The production split between the reactors

was 1 % in prepolymerization, 49 % in loop and 50 % in GPR. Catalyst productivity was 32 kg PP/g cat.

Example 7

5

A continuously operated pilot plant was used to produce PP-homopolymers. The plant comprises catalyst, alkyl, donor, propylene feed systems, a prepolymerization reactor, a loop reactor and a fluidized bed gas phase reactor (GPR).

10

The catalyst, alkyl, donor and propylene were fed to the prepolymerization reactor. The polymer slurry from the prepolymerization reactor was fed to the loop reactor to which also hydrogen and more propylene was fed. The polymer slurry from the loop reactor and additional hydrogen and propylene was fed to the GPR.

15

The polymer formed and unreacted propylene were separated after removal from the GPR.

20

The catalyst used was a highly active and stereospecific ZN-catalyst made according to FI Patent Application No. 963707. The catalyst was contacted with triethylaluminium (TEA) and dicyclopentylmethoxysilane (DCPDMS) (Al/Ti ratio was 250 and Al/Do 40 (mole)) before feeding to the prepolymerization reactor.

25

The catalyst was fed according to U.S. Patent No. 5,385,992 and was flushed with propylene to the prepolymerization reactor. The prepolymerization reactor was operated at a pressure of 53 bar, a temperature of 20 °C and a mean residence time of the catalyst of 7 min.

30

The prepolymerized catalyst propylene and other components were transferred to the loop reactor. The loop reactor was operated at a pressure of 52 bar, a temperature of 85 °C and mean residence time of the catalyst at 1 h. The MFR (2.16 kg, 230 °C) of the PP-homopolymer produced in the loop was adjusted to 7 by controlling the hydrogen feed.

The polymer slurry from the loop reactor was transferred to the GPR. The GPR was operated at a total pressure of 29 bar and a partial propylene pressure of 21 bar. The temperature of the GPR was 80 °C and the mean residence time of the catalyst 1 h. The MFR (2.16 kg, 230 °C) of the PP-homopolymer taken out of the GPR was 7 and it was adjusted by controlling the partial pressure of hydrogen. The production split between the reactors was 1 % in prepolymerization, 53 % in loop and 48 % in GPR. Catalyst productivity was 50 kg PP/g cat.

Example 8

A continuously operated pilot plant was used to produce PP-homopolymer. The plant comprises catalyst, alkyl, donor, propylene feed systems, prepolymerization reactor, loop reactor and a fluidized bed gas phase reactor (GPR).

The catalyst, alkyl, donor and propylene were fed to the prepolymerization reactor. The polymer slurry from the prepolymerization reactor was fed to the loop reactor to which also hydrogen and more propylene was fed. The polymer slurry from the loop reactor and additional hydrogen and propylene was fed to the GPR.

The polymer formed and unreacted propylene were separated after product removal from the GPR.

The catalyst used was a highly active and stereospecific ZN-catalyst made according to U.S. Patent No. 5,234,879. The catalyst was contacted with triethylaluminium (TEA) and dicyclopentylmethoxysilane (DCPDMS) (Al/Ti ratio was 250 and Al/Do 40 (mole)) before feeding to the prepolymerization reactor.

The catalyst was fed according to U.S. Patent No. 5,385,992 and was flushed with propylene to the prepolymerization reactor. The prepolymerization reactor was operated at a 58 bar pressure, a 20 °C temperature and a mean residence time of the catalyst of 7 min.

The prepolymerized catalyst propylene and other components were transferred to the loop reactor.

5 The loop reactor was operated at 57 bar pressure, 80 °C temperature and a mean residence time of the catalyst of 2 h. The MFR (2.16 kg, 230 °C) of the PP-homopolymer produced in the loop was set at 375 via the hydrogen feed.

10 The polymer slurry from the loop reactor was transferred to the GPR. The GPR was operated at a total pressure of 29 bar and a partial propylene pressure of 16 bar. The temperature of the reactor was 80 °C and the mean residence time of the catalyst 2 h. The MFR (2.16 kg, 230 °C) of the PP-homopolymer taken out of the GPR was 450 and it was adjusted by controlling the partial pressure of hydrogen and by controlling the production split between the reactors. The production split was adjusted to comprise 1 % in prepolymerization, 50 % in loop and 49 % in GPR.

15 Example 9

20 A continuously operated pilot plant was used to produce PP-randompolymer. The plant comprises catalyst, alkyl, donor, propylene and ethylene feed systems, a loop reactor and a fluidized bed gas phase reactor (GPR).

25 The catalyst, alkyl, donor and propylene were fed to the prepolymerization reactor. The polymer slurry from the loop reactor and additional hydrogen, propylene and ethylene was fed to the GPR. The polymer formed and unreacted propylene were separated after removal from the GPR.

30 The catalyst used was a highly active and stereospecific ZN-catalyst made according to U.S. Patent No. 5,234,879. The catalyst was prepolymerized with propylene (the mass ratio of PP/cat was 10) in batch according to FI Patent No. 95387. The prepolymerized catalyst was contacted with triethylaluminium (TEA) and dicyclopentyldimethoxysilane (DCPDMS) (Al/Ti ratio was 140 and Al/Do 10 (mole)) before feeding to the loop reactor.

The catalyst was fed according to U.S. Patent No. 5,385,992 and was flushed with propylene to the loop reactor. The loop reactor was operated at a 50 bar pressure, a 75 °C temperature and a mean residence time of the catalyst of 1 h. The MFR (2.16 kg, 230 °C) of the PP-random-polymer produced in the loop adjusted to 4 via the hydrogen feed. The ethylene content was controlled to be 3.5 % w/w via the ethylene feed.

The polymer slurry from the loop reactor was transferred to the GPR. The GPR reactor was operated at a total pressure of 29 bar and a partial propylene pressure of 21 bar. The operational temperature of the GPR was 80 °C and the mean residence time of the catalyst was 1.5 h. The MFR (2.16 kg, 230 °C) of the PP-randompolymer taken out of the GPR was adjusted to 4 via the partial pressure of hydrogen. The ethylene content was controlled to be 3.5 % w/w via partial pressure of ethylene. The production split between the reactors was 55 % in the loop and 45 % in the GPR.

Example 10

A continuously operated pilot plant was used to produce PP-random polymer. The plant comprises catalyst, alkyl, donor, propylene and ethylene feed systems, a loop reactor and a fluidized bed gas phase reactor (GPR).

The catalyst, alkyl, donor and propylene were fed to the prepolymerization reactor. The polymer slurry from the loop reactor and additional hydrogen and propylene was fed to the GPR. The polymer formed and unreacted propylene were separated after removal from GPR.

The catalyst used was a highly active and stereospecific ZN-catalyst made according to U.S. Patent No. 5,234,879. The catalyst was prepolymerized with propylene (the mass ratio of PP/cat was 10) in batch according to Finnish Patent No. 95387. The prepolymerized catalyst was contacted with triethylaluminium (TEA) and dicyclopentyl dimethoxysilane (DCPDMS) (Al/Ti ratio was 135 and Al/Do 10 (mole)) before feeding to the loop reactor.

The catalyst was fed according to U.S. Patent No. 5,385,992 and was flushed with propylene to the loop reactor. The loop reactor was operated at a pressure of 50 bar, a temperature of 75 °C and a mean residence time of the catalyst of 1 h. The MFR (2.16 kg, 230 °C) of the PP-randompolymer produced in the loop was set at 0.2 by adjusting the hydrogen feed. The ethylene content was 3.5 % w/w and adjusted by controlling the ethylene feed.

The polymer slurry from the loop reactor was transferred to the GPR. The GPR reactor was operated at a total pressure of 29 bar and a partial propylen pressure of 21 bar. The operational temperature was 80 °C and the mean residence time of the catalyst was 1.5 h. The MFR (2.16 kg, 230 °C) of the PP-random polymer taken out of the GPR was adjusted to 3 by controlling the partial pressure of the hydrogen. The ethylene content was set at 1.8 % w/w by adjusting the production split between the reactors. The desired ethylene content was achieved at a production split of 40 % in loop and 60 % in GPR.

The prepolymerization reactor was operated at a 56 bar pressure and a 20 °C temperature. The loop reactor was operated at a 55 bar pressure and a 75 °C temperature. The MFR (2.16 kg, 230 °C) of the random-PP produced in the loop was below 0.1 and the ethylene content was adjusted to 3.5 % w/w by controlling the ethylene feed.

The GPR reactor was operated at a 35 bar pressure and a 80 °C temperature. The MFR (2.16 kg, 230 °C) of the PP-copolymer taken out of the GPR was 0.3 and adjusted by the partial hydrogen pressure. The ethylene content was set at 1.8 % w/w by adjusting the production split between the reactors.

Ethylene in the loop outlet was recovered from the flash gases and circulated back to the loop reactor. Propylene in the outlet of the GPR was recovered and fed to the loop reactor after removal of hydrogen. The once-through conversions of propylene and ethylene were 83 % and 84 %, respectively.

Example 11

A continuously operated pilot plant was used to produce PP-copolymer with good impact and creep properties. The plant comprises catalyst, alkyl, donor, propylene and ethylene feed systems, a prepolymerization reactor, a loop reactor and two fluidized bed gas phase reactors (GPR).

The catalyst, alkyl, donor and propylene are fed to the prepolymerization reactor. The polymer slurry from the prepolymerization reactor is fed to a loop reactor to which also hydrogen, ethylene and additional propylene are fed.

The polymer slurry from the loop reactor and additional hydrogen and propylene are fed to the first GPR. The polymer from the first GPR is fed to the second GPR. Ethylene, some hydrogen and additional propylene was fed to the second GPR. The polymer formed and unreacted propylene are separated after removal from the second GPR.

The catalyst used is a highly active and stereospecific ZN-catalyst made according to U.S. Patent No. 5,234,879. The catalyst is contacted with triethylaluminium (TEA) and dicyclopentylmethoxysilane (DCPDMS) (Al/Ti ratio is 150 and Al/Do 10 (mole)) before feeding to the prepolymerization reactor.

The catalyst is fed according to U.S. Patent No. 5,385,992 and is flushed with propylene to the loop reactor. The prepolymerization reactor is operated at a pressure of 51 bar, a temperature of 20 °C and a mean residence time of the catalyst of 7 min.

The loop reactor is operated at a 50 bar pressure, a 75 °C temperature and a mean residence time of the catalyst of 1 h. The MFR (2.16 kg, 230 °C) of the PP-randompolymer produced in the loop is adjusted to 7 by controlling the hydrogen feed. The ethylene content is adjusted to 3.5 % w/w by using the ethylene feed as a control means.

The polymer slurry from the loop reactor is transferred to the first GPR. The first GPR reactor is operated at a total pressure of 29 bar and a partial propylene pressure of 21 bar.

The operational temperature is 80 °C and the mean residence time of the catalyst 1.5 h. The MFR (2.16 kg, 230 °C) of the PP-randompolymer taken out of the GPR adjusted to 10 by using the partial hydrogen pressure. The ethylene content is set at 2 % w/w by adjusting the production split between the reactors.

5

The polymer from the first GPR is transferred to the second GPR. The second GPR is operated at a total pressure of 10 bar and a partial monomer pressure of 7 bar. The operational temperature is 80 °C and mean residence time of the catalyst 1.5 h. The MFR (2.16 kg, 230 °C) of the PP-copolymer taken out of the GPR is adjusted to 7 via the partial pressure of the hydrogen. The ethylene content is set at 10 % w/w by adjusting the partial pressure of ethylene and by controlling the production split between the reactors.

10

The desired properties are achieved with a production split of 1 % in prepolymerization, 40 % in loop and 40 % in the first GPR and 19 % in the second GPR.

15

Example 12

A continuously operated pilot plant was used to produce very soft PP-copolymer. The plant comprises catalyst, alkyl, donor, propylene and ethylene feed systems, prepolymerization reactor, loop reactor and a fluidized bed gas phase reactor (GPR).

20

The catalyst, alkyl, donor and propylene were fed to the prepolymerization reactor. The polymer slurry from the prepolymerization reactor was fed to a loop reactor ton which also hydrogen, ethylene and additional propylene was fed.

25

The polymer slurry from the loop reactor and additional ethylene, hydrogen and propylene were fed to the GPR. The formed polymer and unreacted monomers were separated after removal from GPR.

30

The catalyst used was a highly active and stereospecific ZN-catalyst made according to U.S. Patent No. 5,234,879. The catalyst was contacted with triethylaluminium (TEA) and

dicyclopentyl-dimethoxysilane (DCPDMS) (Al/Ti ratio was 150 and Al/Do 10 (mole)) before feeding to the prepolymerization reactor.

5 The catalyst was fed according to U.S. Patent US-5,385,992 and was flushed with propylene to the loop reactor. The prepolymerization reactor was operated at a 51 bar pressure, a 20 °C temperature and a mean residence time of the catalyst of 7 min.

10 The loop reactor was operated at a pressure of a 50 bar, a temperature of 75 °C temperature and mean residence time of the catalyst at 1 h. The MFR (2.16 kg, 230 °C) of the PP-random-polymer produced in the loop was controlled to be 4 via hydrogen feed. The ethylene content was adjusted to 3.8 % w/w by controlling the ethylene feed.

15 The polymer slurry from the loop reactor was transferred to the first GPR. The first GPR reactor was operated at a total pressure of 29 bar and a partial propylene pressure of 21 bar. The operational temperature was 80 °C and the mean residence time of the catalyst 1.2 h. The MFR (2.16 kg, 230 °C) of the PP-randompolymer taken out of the GPR was set at 2.5 by adjusting the partial hydrogen pressure. The ethylene content was set at 8 % w/w by adjusting production split between the reactors and the partial pressure of ethylene.

20 Desired properties are achieved with a production split of 1 % in prepolymerization, 45 % in loop and 55 % in the GPR.

25 The polymer from the GPR could have been transferred to another GPR to produce even softer PP copolymer by having even higher partial pressure of ethylene in the second GPR.

Example 13

30 A continuously operated pilot plant was used to produce PP-copolymer with good creep properties. The plant comprises catalyst, alkyl, donor, propylene and ethylene feed systems, a prepolymerization reactor, a loop reactor and a fluidized bed gas phase reactor (GPR).

The catalyst, alkyl, donor and propylene were fed to the prepolymerization reactor. The polymer slurry from the prepolymerization reactor was fed to the loop reactor to which also hydrogen, additional propylene was fed.

5 The polymer slurry from the loop reactor was fed to a flash tank wherein monomers and polymer were separated. The polymer from the flash tank was fed to the GPR. Propylene from flash tank was fed to the GPR after removal of hydrogen. Ethylene, additional hydrogen and additional propylene were fed to the GPR.

10 The catalyst used was a highly active and stereospecific ZN-catalyst made according to U.S. Patent 5.234.879. The catalyst was contacted with triethylaluminium (TEA) and dicyclopentylmethoxysilane (DCPDMS) (Al/Ti ratio was 140 and Al/Do 10 (mole)) before feeding to the prepolymerization reactor.

15 The catalyst was fed according to U.S. Patent No. 5,385,992 and was flushed with propylene to the loop reactor. The prepolymerization reactor was operated at a 51 bar pressure, a 20 °C temperature and a mean residence time of the catalyst of 7 min.

The loop reactor was operated at a 50 bar pressure, a 75 °C temperature and a mean residence time of the catalyst of 1 h. The MFR (2.16 kg, 230 °C) of the PP-randompolymer produced in the loop was set at 10 by adjusting the hydrogen feed.

25 The GPR reactor was operated at a total pressure of 29 bar and a partial propylene pressure of 16 bar. The operational temperature was 80 °C and the mean residence time of the catalyst 1.1 h. The MFR (2.16 kg, 230 °C) of the PP-copolymer taken out of the GPR was adjusted to 5 via the partial hydrogen pressure and via the production split between the reactors. The ethylene content was adjusted to 3.5 % w/w by controlling the production split between the reactors and partial pressure of ethylene.

30 Desired properties are achieved with production split of 1 % in prepolymerization, 40 % in loop and 59 % in the GPR.

The polymer from the GPR could have been transferred to another GPR to produce PP copolymer with better impact properties by having even higher partial pressure of ethylene in the second GPR.

In the Claims:

1. A process for preparing propylene homopolymers and copolymers, which comprises polymerizing propylene optionally with comonomers in the presence of a catalyst at elevated temperature and pressure in at least one slurry reactor and at least one gas phase reactor, the polymerization product of at least one slurry reactor, containing unreacted monomers, being directly conducted to a first gas phase reactor essentially without recycling of the unreacted monomers to the slurry reactor.
2. The process according to claim 1, wherein the polymerization product of the slurry reactor comprises polymeric substances selected from the group consisting of polypropylene, propylene copolymers and mixtures of polypropylene and propylene copolymers.
3. The process according to claim 1 or 2, wherein the slurry reactor comprises a loop reactor and wherein the concentration of propylene in the reaction medium is over 60 wt-% and the product forms a particulate form.
4. The process according to any of claims 1 to 3, wherein the slurry reactor is operated at a temperature in the range of 60 to 80 °C for preparing random or ter-copolymers.
5. The process according to any of claims 1 to 3, wherein the slurry reactor is operated at a temperature in the range of 80 °C to the critical temperature of the reaction medium.
6. The process according to any of claims 1 to 3, wherein the slurry reactor is operated at a temperature higher than the critical temperature of the reaction medium and below the softening temperature of the polymer.
7. The process according to any of claims 1 to 6, wherein the slurry reactor is operated at a pressure in the range of 35 to 100 bar.

8. The process according to any of the preceding claims, wherein the polymerization product is conducted from the slurry reactor to the first gas phase reactor via a direct pipeline.

5 9. The process according to any of the preceding claims, wherein the reaction medium of the polymerization product is evaporated before the polymerization product is fed into a first gas phase reactor.

10 10. The process according to claim 9, wherein the polymerization product is conducted from the slurry reactor to the first gas phase reactor via a jacketed pipe line heated by steam for providing at least a part of the energy needed for evaporation of the reaction medium.

15 11. The process according to any of the preceding claims, wherein the polymerization product fed to the first gas phase reactor contains copolymers comprising > 0.5 wt-%, preferably 2 to 16 wt-%, of at least one comonomer.

20 12. The process according to claim 11, wherein the polymerization product is copolymerized in the first gas phase reactor with additional comonomers to increase the comonomer content.

13. The process according to claim 12, wherein the comonomer content is increased up to 20 wt-%.

25 14. The process according to any of claims 1 to 13, wherein polymerization in the first gas phase reactor is carried out without additional monomer feed.

30 15. The process according to any one of the preceding claims, wherein a polymerization product is recovered from the gas phase reactor to provide improved properties, such as stiffness, creep properties, or softness.

16. The process according to claim 15, wherein the polymerization product is subjected to copolymerization in the presence of comonomers to provide a third polymer product with improved impact strength properties.

5 17. The process according to claim 16, wherein the copolymerization is carried out in a second gas phase reactor arranged in series with the first gas phase reactor.

10 18. The process according to claim 16 or 17, wherein the first modified polymer is recovered and subjected to further copolymerization to provide a fourth polymer product having properties of improved stiffness, impact balance or stress whitening or white blush properties.

15 19. The process according to claim 18, wherein the further copolymerization reaction is carried out in a third gas phase reactor arranged in series with the second gas phase reactor.

20 20. The process according to claim 18 or 19, wherein the second modified polymer is subjected to at least one further copolymerization reaction in at least one further reactor.

25 21. The process according to any of the preceding claims, wherein at least part of the unreacted monomers are recovered from the second and/or third gas phase reactor and recycled back to the previous gas phase reactor(s).

30 22. The process according to any of the preceding claims, wherein the unreacted monomers recovered from the first gas phase reactor are recycled back to the gas phase reactor.

23. The process according to any of the preceding claims, wherein the unreacted monomers recovered from the first gas phase reactor are recycled back to the slurry reactor.

35 24. The process according to any of the preceding claims, wherein a part of the unreacted monomers recovered from the first gas phase reactor is recycled back to the slurry reactor.

25. The process according to claim 24, wherein the amount of monomers recycled comprises 1 to 65 wt-% of the amount of monomers in the feed of the slurry reactor.

26. The process according to any of the preceding claims, wherein the production rate of the slurry reactor is 10 to 70 wt-%, preferably 20 to 65 wt-%, in particular 40 to 60 wt-%, of the total production rate of the slurry and the first gas phase reactor.

27. The process according to any of the preceding claims, wherein hydrogen is used in at least one reactor as a molar mass modifier.

28. The process according to any of the preceding claims, wherein the catalyst used is prepolymerized before feeding it into the process.

29. A process for preparing propylene homopolymers and copolymers, which comprises the steps of

- subjecting propylene optionally with comonomers to polymerization in the presence of a catalyst at elevated temperature and pressure in at least one slurry reactor to produce a first polymerization product comprising propylene polymer and unreacted monomers,
- recovering the polymer and the unreacted monomers,
- feeding the polymer to at least one gas phase reactor,
- feeding essentially all of the unreacted monomers to said gas phase reactor,
- subjecting the polymers and the unreacted monomers to polymerization in said gas phase reactor to produce a second polymerization product containing propylene polymer and gaseous substances, and
- recovering the propylene polymer.

30. The process according to claim 29, wherein the propylene polymer is fed to a further gas phase reactor for copolymerization.

31. The process according to claim 29 or 30, wherein hydrogen is used as molar mass modifier in at least one of the reactors.

32. The process according to any of claims 29 to 31, wherein the polymerization in gas phase is carried out essentially without additional feed of monomers.

33. A process for preparing propylene copolymers, which comprises the steps of

- 5 – polymerizing propylene with comonomers in the presence of a catalyst at an elevated temperature of 60 to 85°C and at an elevated pressure in at least one slurry reactor and at least one gas phase reactor, at least 10 % of the polymer product being produced in the gas phase reactor(s),
- 10 – recovering from the slurry reactor a copolymerization product containing unreacted monomers and
- conducting the copolymerization product to a first gas phase reactor essentially without recycling of the unreacted monomers to the slurry reactor before the gas phase reactor.

15 34. The process according to claim 33, wherein the slurry reactor is operated at a temperature in the range of 60 to 75 °C for preparing random and ter-copolymers.

35. The process according to claim 33, wherein the slurry reactor is operated at a temperature in the range of 75 to 85 °C for improved activity and comonomer randomness.

20

36. The process according to claim 33, wherein the polymerization product is subjected to copolymerization in the presence of comonomers to provide a first modified polymer with improved softness properties.

25 37. A process for preparing propylene polymers, which comprises the steps of

- polymerizing propylene with comonomers in the presence of a catalyst at an elevated temperature of at least 80 °C and at an elevated pressure in at least one slurry reactor and at least one gas phase reactor, at least 40 % of the polymer product being produced in the gas phase reactor(s),
- 30 – recovering from the slurry reactor a polymerization product containing unreacted monomers and

- conducting the polymerization product to a first gas phase reactor essentially without recycling of the unreacted monomers to the slurry reactor before the gas phase reactor.

38. The process according to claim 37, wherein the polymerization product is subjected to copolymerization in the presence of comonomers to provide a modified polymer product with improved impact properties.

39. The process according to claim 37, wherein the copolymerization is carried out in a second gas phase reactor arranged in series with the first gas phase reactor.

40. A propylene homo- or copolymer prepared according to a process according to any of claims 1 to 39.

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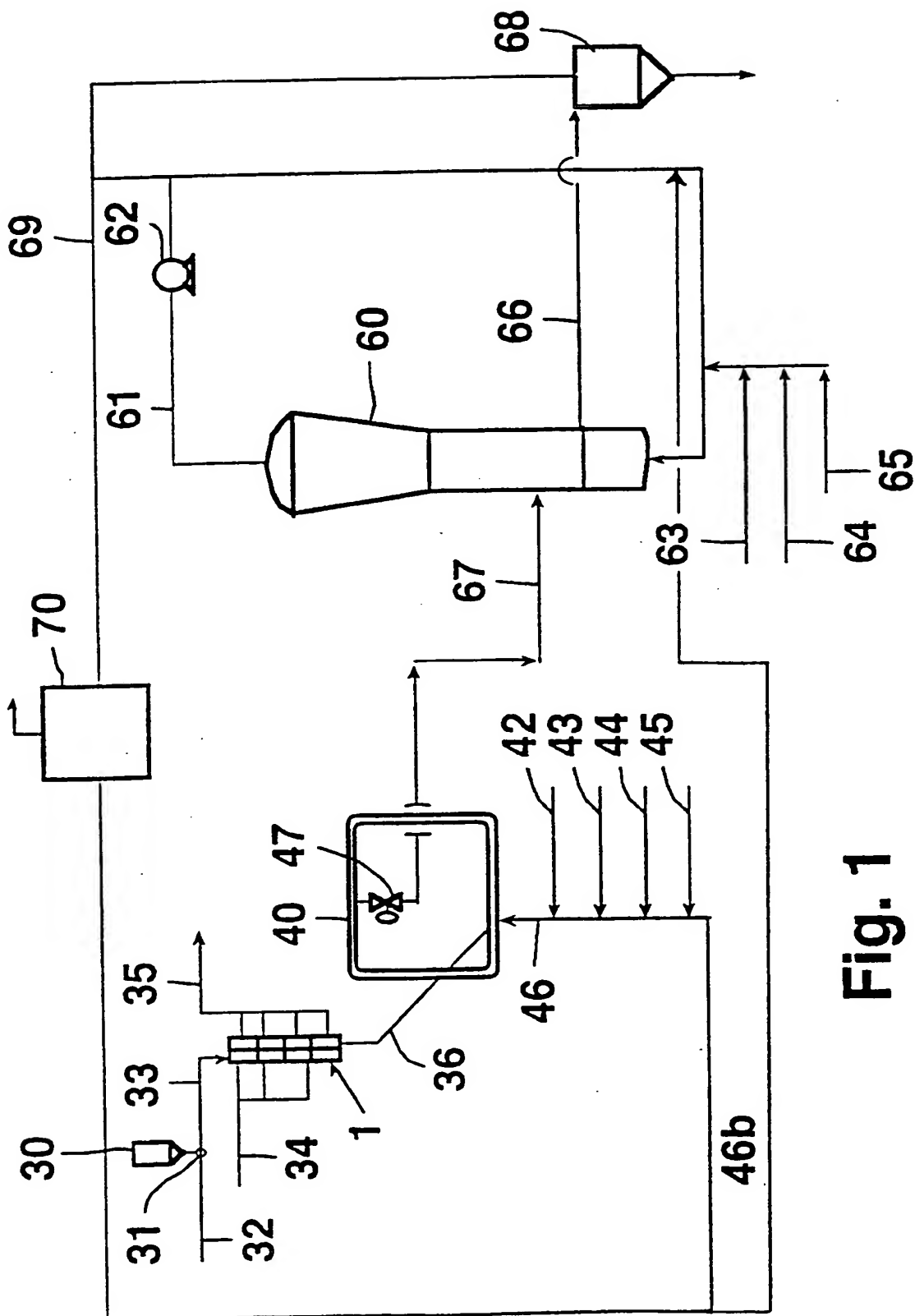


Fig. 1

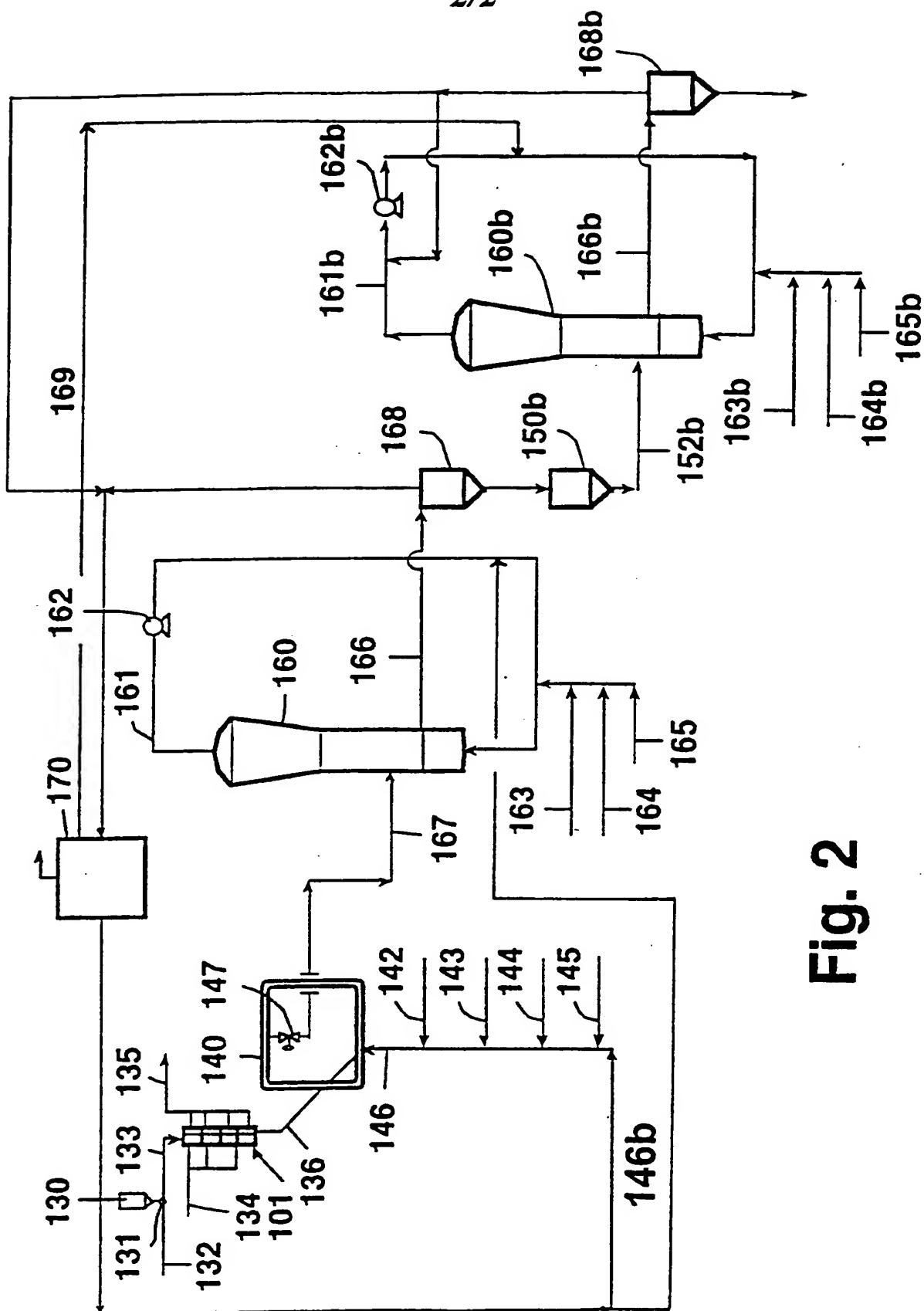


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00554

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08F 297/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9713790 A1 (BOREALIS A/S), 17 April 1997 (17.04.97), abstract, claims --	1-40
A	US 4740551 A (E. GORDON FOSTER), 26 April 1988 (26.04.88), abstract, example 1, claims 1-2 --	1-40
A	US 4740550 A (E. GORDON FOSTER), 26 April 1988 (26.04.88), abstract, examples 1-2, claims 1-5, 7-8 --	1-40



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
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"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

21 Sept 1998

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Name and mailing address of the ISA:

Swedish Patent Office
Box 5055, S-102 42 STOCKHOLM
Facsimile No. +46 8 666 02 86

Authorized officer

Monika Bohlin
Telephone No. +46 8 782 25 00

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 98/00554

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	File WPI, Derwent accession no. 91-146186, Mitsubishi Kasei Corp: "Prepn. of propylene- ethylene block copolymer in continuous process - using classification method to separate fine and coarse polypropylene particles in slurry, etc."; & JP,A,3084014, 910409 DW9120, abstract --	1-40
A	File WPI, Derwent accession no. 83-803582, Mitsubishi Chem Ind Ltd: "Polyolefin mfr. - by polymerising olefin in liq. propylene, passing slurry to vaporising tank, collecting sepd. powdery polyolefin"; & JP,A,58065710, 830419 DW8344; JP,A,3032561B, 910513 DW9123, abstract -- -----	1-40

INTERNATIONAL SEARCH REPORT
Information on patent family members

27/07/98

International application No.

PCT/FI 98/00554

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				FI	954814 A	11/04/97

US	4740551	A	26/04/88	NONE		

US	4740550	A	26/04/88	NONE		

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